Magnetic Polarons in Dilute Ferromagnetic Oxide Films and Nanoparticles

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Abstract

The d^0 ferromagnetism in oxide films and nanoparticles without 3d elements and long-range magnetic order at concentrations of magnetic cations below the percolation limit with Curie temperature exceeding 300K is not explained on the present understanding of magnetism in solids. It is shown that these arise in nanostructure solids when two degenerate spin-polarized macro states of the system through coupling to zero-point phonon removes the degeneracy and increases the binding energy of the system by a small amount. The coupling through quantum tunnelling persists even in the presence of thermal fluctuations until the fraction of recoilless transitions in the ground state of the lattice vanishes. This accounts for its weak intensity, universality and existence over a wide temperature range.

Key Words: d^0 magnetism, Spin-polarized transport, Zero-point phonon

I. INTRODUCTION

The electrical transport and magnetic studies in some undoped- and doped- oxides at nanoscale have presently invoked immense interest due to their ability to switch magnetization under small magnetic fields which is central to the technology of spintronic applications [1, 2]. The observation of high-temperature ferromagnetism in HfO_2 [3] led to extensive studies of this kind by many others. On the basis of Zener model of ferromagnetism Dietl et al. [4] predicted that Mn-doped ZnO and GaN could exhibit ferromagnetism above room temperature. It is now believed by many researchers that the predictions of room temperature ferromagnetism (RTF) based on Zener model in dilute magnetic semiconductors is not applicable due to unrealistic assumptions. In particular the transport and magnetoresistance in manganites based on double exchange mechanism are not explained satisfactorily using models like Jahn-Teller polaron [5] and two-fluid [6] due to the large size of transfer integral. This is overcome in the correlated polaron (CP) model through coupling of electrons to phonons in mixed-valence ionic compounds [7,8]. We show here that CP model applies to transport and ferromagnetism in nanostructure oxides in which quantum tunnelling by charge carriers leads to Mott-like transition reported in many nanostructure systems [9,10].

The magnetization of the doped material $[\text{A}_{1-x}\text{M}_x][\text{O}_{1-\delta}]$ depends on (i) the dopant, M , (ii) its concentration, x , (iii) the matrix, A , and (iv) the oxygen deficiency, δ . It falls steeply as x is increased and vanishes for $x > 0.25$. An estimate of critical temperature on the charge transfer mechanism gives the exchange energy between the cation spin S and spin s of the electron in the donor band of the order of 4.0 eV for $T_c = 500$ K [11]. We present here an explanation based on phase coherence amongst zero-point phonon-coupled spins in CP model that gives reasonable values of J_{sd} of a few meV.

The as-deposited films of Al and Ni Co-doped ZnO films are not magnetic but develop RTF on magnetic annealing [9]. The SnO_2 films with and without Co doping, annealed and as grown, show localization of the charge carriers at low temperature [12]. In cobalt-doped TiO_2 film, a gate voltage of a few volts changes carriers from paramagnetic to ferromagnetic state with electron density of $10^{14}/\text{cm}^2$ [1]. We show that the transport equation derived on the CP model satisfactorily accounts for all these experimental results.

II. THE CORRELATED POLARON (CP) MODEL

The itinerancy in the CP model arises through phonon-induced charge-spin ($e\downarrow$) exchange in ionic compounds where an anion or a cation exists in mixed-valence state on crystallographic equivalent sites and form two

degenerate macro- states, Ψ_1 and Ψ_2 , obtained by the interchange of $(e\downarrow)$, $O^{-1}\uparrow + O^{-2} \leftrightarrow O^{-2} + O^{-1}\uparrow$. The degeneracy is removed on coupling to a phonon of energy $\hbar\omega_0$ with gain in energy ε_p [7, 8]. The electron transfer occurs from one site to another as in the Zener model but with much reduced amplitude of the transfer integral which can be expressed as $t \sim \hbar\omega_0 \exp(-\varepsilon_p / \hbar\omega_0)$. For a typical value of $\hbar\omega_0 = 25$ meV and $\varepsilon_p = 30$ meV, $t \sim 7.5$ meV, an order of magnitude smaller than 0.20 eV used in the JT and two-fluid models for manganites[7].

Including the contribution from the zero-point phonons the dc resistivity at temperature T in the adiabatic approximation is [7]

$$\rho_1(T) = \frac{A}{n} (T + \theta_E) \cosh^2 \left[\frac{\varepsilon_p}{2k(T + \theta_E)} \right] \quad (1)$$

where $A = \xi k / (e^2 a^2 v_{ph})$. Here ξ is a geometrical factor of order unity, k is Boltzmann constant, n is the charge carrier density, a is the jump distance, v_{ph} is the phonon frequency; $k\theta_E$ is the zero-point energy of the Einstein oscillator. The mobility from Eq.(1) is

$$\mu(T) = \frac{eD}{(T + \theta_E)} \sec h^2 \left\{ \frac{\varepsilon_p}{2(T + \theta_E)} \right\} \cosh^2 \left\{ \frac{\varepsilon_p}{\theta_E} \right\} \quad (2)$$

where $D = a^2 v_{ph}$ and $k = 1$. In Eq.(1) the number n of the mobile correlated charge carriers is determined by the number of mixed charge states of oxygen. The probability of recoilless zero-point coherent spin-charge transfer in the exchange $\Psi_1 \leftrightarrow \Psi_2$ depends on the dimensionality of the solid and is given by

$$\rho(T) = \rho_1(T) \left[1 - \frac{1}{\exp(h\nu_{ph}/kT) - 1} \right]^{d/3} \quad (3)$$

where d represents the dimensionality of the solid, $d=3$ for 3D, 2 for 2D and 1 for 1D. This arises from recoilless zero-point phase coherent spin-charge transfer in the exchange $\Psi_1 \leftrightarrow \Psi_2$ [13]. This transport vanishes at T_c ,

$$k_B T_c = (h\nu_{ph} / \ln 2) = 1.442 h\nu_{ph} \quad (4)$$

The expression for resistivity in Eq.(1) holds for $T < \theta_D/4$ ($\theta_D = h\nu_{ph}/k$), when the Frank-Cordon transitions do not occur. In that case a metal to insulator Mott-transition occurs at

$$T_M = [\varepsilon_p / 1.544 - \theta_E] \quad (5)$$

III EXPERIMENTAL RESULTS

The observed $\rho(T)$ curves for doped and undoped SnO_2 films [13] is shown in Fig.(1a) with (i) undoped SnO_2 film,

Fig. 1 $\rho(T)$ curves using Eq.3 and parameters given in table 1 are compared with experiment. (a) Co-doped SnO_2 film [12], (b) Zn-Al-Ni film (as grown) from [9] and (c) Co-doped TiO_2 film from [1]

(ii) as-grown Co-doped SnO_2 film and (iii) annealed Co-doped SnO_2 film., Fig. (1b) gives $\rho(T)$ for as grown $\text{Zn}_{0.91}\text{Al}_{0.07}\text{Ni}_{0.02}\text{O}_2$ film from [9] and in Fig. (1c) $\rho(T)$ is given for $\text{Ti}_{0.90}\text{Co}_{0.10}\text{O}_2$ film without gate voltage, $V_G=0$ from [1]. $\rho(T)$ curves using Eq.(3) with parameters in table1 show good agreement.

The values of A/n , n , θ_E , ϵ_p , d with $\xi=1$ are obtained from Eq.(3), while T_c and T_M are from Eq.(4) and (5) $2\theta_E$ for annealed films is 120K for each of the three compositions while ϵ_p is nearly the same and lies between 340K and 400K. The frequency, ν_{ph} , however varies significantly. It is 222 cm^{-1} for SnO_2 , 275 cm^{-1} for ZnO and 402 cm^{-1} for TiO_2 doped films. The electron density n is highest for Al-Ni doped ZnO film, $1.9 \times 10^{22}/\text{cm}^3$. In Fig. (1b) for as grown Zn-Al-Ni film there is departure of observed $\rho(T)$ from theory, for low temperature indicating that below the Mott temperature, $T_M=222\text{K}$, dimensionality, d , of the charge transport changes from 3 to 1 with reduced electron charge density n .

Table I The parameters A/n , n , θ_E , ϵ_p , T_M , T_c , ν_{ph} and d obtained from the resistivity curve using Eqs. 1, 3, 4 and 5.

Composition Film(F)	A/n $\Omega\text{-cmK}^{-1}$	n (cm^3)	$2\theta_E$ (K)	ϵ_p (K)	T_M (K)	T_c (K)	ν_{ph} (cm^{-1})	d	Ref
$\text{Sn}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}(\text{F})$ Annealed	5.88×10^{-3}	1.70×10^{19}	120	400	199	480	222	1	11
$\text{Sn}_{0.95}\text{Co}_{0.05}\text{O}_{2-\delta}(\text{F})$ as grown	2.0×10^{-3}	5.0×10^{19}	130	400	194	440	202	1	11
$\text{SnO}_{2-\delta}(\text{F})(\text{undoped})$	6.94×10^{-5}	1.44×10^{21}	200	350	127	480	222	1	11
$\text{Ti}_{0.90}\text{Co}_{0.10}\text{O}_2(\text{F})$	1.92×10^{-4}	5.0×10^{20}	120	340	222	870	402	1	1
$\text{Zn}_{0.91}\text{Al}_{0.07}\text{Ni}_{0.02}\text{O}(\text{F})$ as grown	3.13×10^{-5}	2.95×10^{21}	165	470	222	466	216	3	9
$\text{Zn}_{0.91}\text{Al}_{0.07}\text{Ni}_{0.02}\text{O}(\text{F})$ annealed	5.88×10^{-6}	1.9×10^{22}	120	345	163	595	275	3	9

A model of transport based on long range spin coupling through zero-point phonons forming magnetic polaron is proposed to account for the universality, low intensity and high critical temperature of the magnetic phase in nanostructure oxide systems.

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